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2. REPORT DATE
November 3, 19943. REPORT TYPE AND DATES COVERED
Preprint of article

4. TITLE AND SUBTITLE

Density Functional Studies of Decomposition Processes
of Energetic Molecules

5. FUNDING NUMBERS

C N00014-91-J-4057

6. AUTHOR(S)

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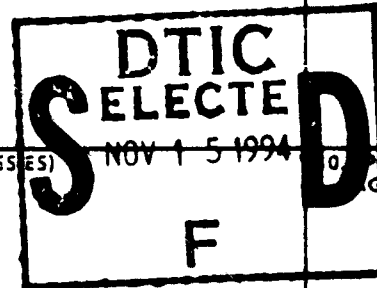
Dr. Richard S. Miller

R&T Code 4131D02

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of New Orleans
Department of Chemistry
New Orleans, Louisiana 701488. PERFORMING ORGANIZATION
REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
Code 333
800 N. Quincy Street
Arlington, VA 2221710. SPONSORING/MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release.
Unlimited distribution138 94-35073

13. ABSTRACT (Maximum 200 words)

Nonlocal density functional theory is an effective means for determining the energetics and elucidating the mechanisms of the decomposition processes of molecules of real chemical interest and significance. It should be viewed as another practical tool that is available for this purpose, a useful addition to existing experimental techniques, but with the extremely important advantage that it can be applied to proposed molecules that may not yet have been synthesized or isolated. In this article decomposition energetics of some nitramines and nitrotriazoles are presented and discussed.

14. SUBJECT TERMS

nonlocal density functional calculations, decomposition
energetics, nitramines, nitrotriazoles, impact sensitivity

15. NUMBER OF PAGES

12

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

Unclassified

18. SECURITY CLASSIFICATION
OF THIS PAGE

Unclassified

19. SECURITY CLASSIFICATION
OF ABSTRACT

Unclassified

20. LIMITATION OF ABSTRACT

Unlimited

Density Functional Studies of Decomposition Processes of Energetic Molecules

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1. INTRODUCTION

For the purposes of interpreting and predicting chemical reactivity, *ab initio* Hartree-Fock computations are often quite satisfactory. These yield one-electron properties, such as the molecular electrostatic potential, to first-order accuracy [1-5], which frequently suffices to identify, for example, sites for electrophilic and/or nucleophilic attack [2, 5]. Quantities related to the electrostatic potential on the molecular surface have also been related to a variety of condensed phase macroscopic properties, including pK_a 's, heats of vaporization, boiling points, critical constants, solubilities, etc. [6, 7].

However Hartree-Fock procedures, which by definition do not include correlation contributions, are generally inadequate for calculating dissociation energies and activation barriers [8]. Correlated or many-body techniques can of course be used for these purposes, but they are very demanding in terms of computer resources. Density functional (DF) methods, even at relatively low levels, do take account of electronic correlation and therefore can represent accurate and practical means for determining reaction energetics. Local DF procedures are often satisfactory for computing activation barriers [9-11], but it is well-known that they overestimate dissociation energies [12-15], for which non-local DF approaches are necessary.

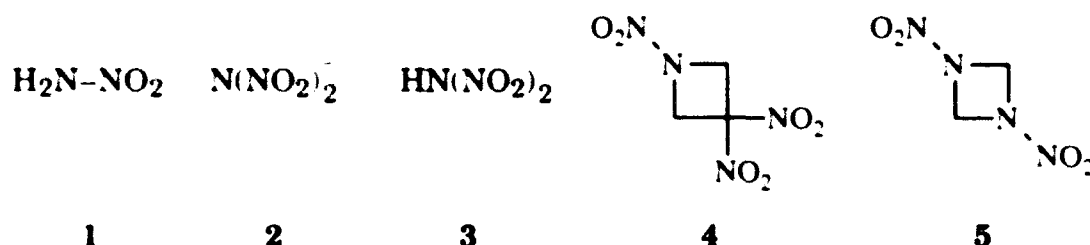
In recent years, we have made considerable use of the latter in investigating possible decomposition routes of various energetic molecules, primarily nitramines; these results will be summarized in section 2. Our current focus is on how structural and electronic factors affect the

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sensitivities toward impact of heterocyclic nitro derivatives; this will be discussed in section 3.

2. POSSIBLE DECOMPOSITION STEPS OF SOME NITRAMINES

Nitramide, 1, is the simplest possible nitramine and is included for that reason. However 2 - 5 are of practical interest as energetic materials. 2 - 4 are known, and efforts are underway to prepare 5.



All of the results to be presented in this section were obtained with the program deMon [16], using the Gaussian DZVPP basis set (approximately equivalent to 6-31G**). The exchange and correlation functionals were expressed in terms of the generalized gradient approximations (GGA) [17, 18]. The energy values that do not include zero-point corrections are indicated by an asterisk.

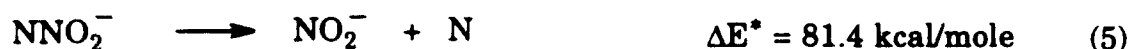
(a) $\text{H}_2\text{N}-\text{NO}_2$ (1) [19]:

ΔE for the dissociation represented by eq. (1) is very similar to the activation barrier for the nitro-nitrite rearrangement, eq. (2). Accordingly these processes should be competitive.



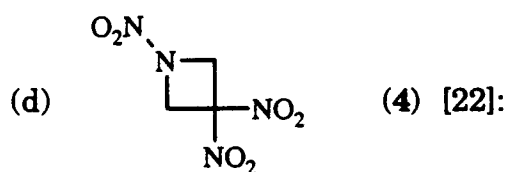
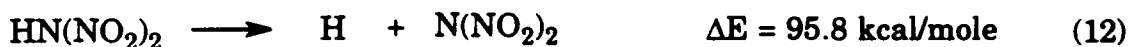
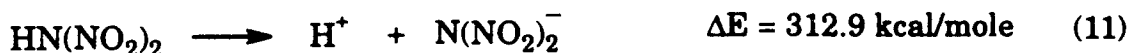
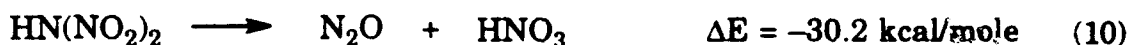
(b) $\text{N}(\text{NO}_2)_2$ (2) [20]:

Of the three possible N-N bond-breaking reactions, to produce NO_2^+ , NO_2^- or NO_2 , the lowest energy requirement is for that shown in eq. (3). Some possible subsequent steps are shown as eqs. (4) - (7). From eqs. (3), (4) and (7), one can obtain the overall ΔE to the observed products N_2O and NO_3^- , eq. (8).

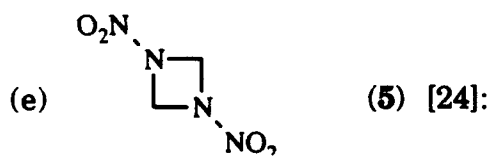
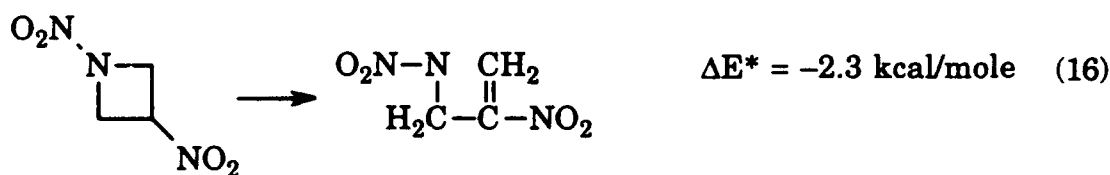
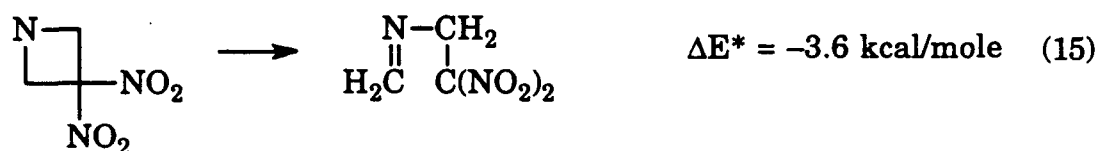
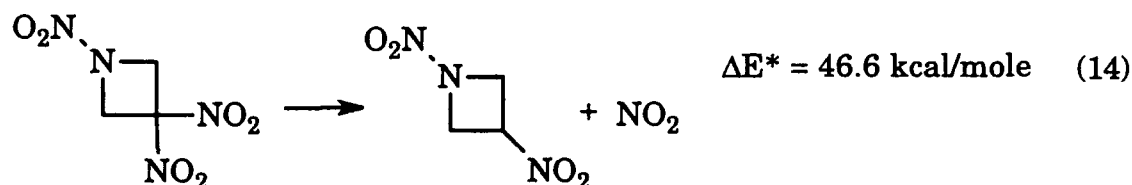
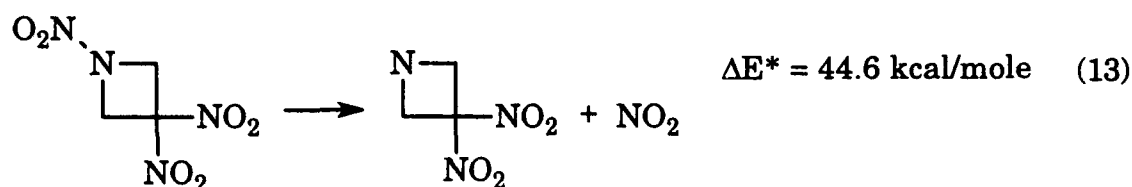


(c) $\text{HN}(\text{NO}_2)_2$ (3) [21]:

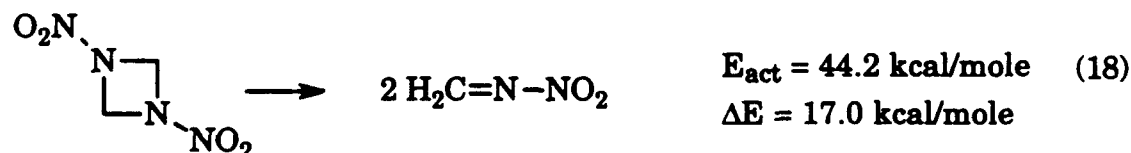
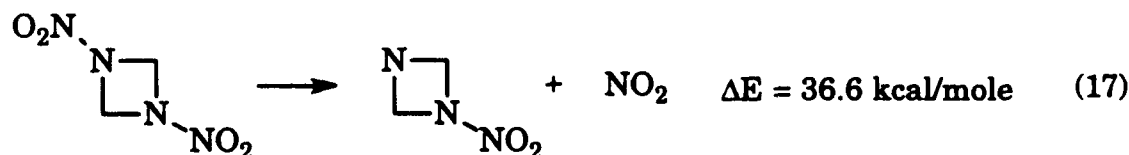
In analogy to 2, the most facile N-N bond rupture is that which yields NO_2 , eq. (9). The overall ΔE for the formation of N_2O and HNO_3 , eq. (10), is -30.2 kcal/mole. Eqs. (11) and (12) show that homolytic dissociation of the H-N bond is much easier than heterolytic.



The loss of the first NO_2 from 4 could occur on either the nitrogen or the doubly-substituted carbon, eqs. (13) and (14). Somewhat surprisingly, the energy requirements are quite similar, as are those for the ring-opening that has been suggested as being the next step [23], eqs. (15) and (16). However the loss of a second NO_2 does differentiate energetically between the two pathways [22].



The N-NO₂ dissociation energy of 5, eq. (17), is a relatively low 36.6 kcal/mole, somewhat less than the activation barrier for ring fragmentation, eq. (18).

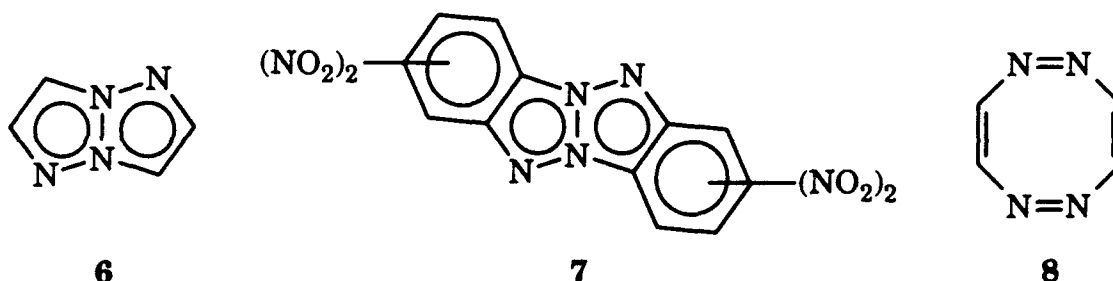


The preceding brief summaries present the key points of more extensive studies that are described in greater detail in the original sources. In all instances, the calculated DF-GGA/DZVPP results are in satisfactory agreement with the limited experimental data that are available.

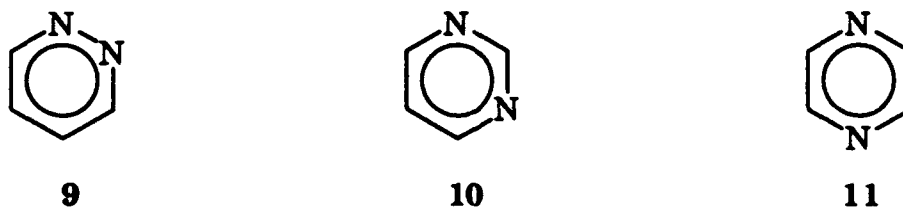
3. SENSITIVITIES OF HETEROCYCLIC NITRO DERIVATIVES

There is currently a great deal of interest, as potential energetic materials, in heterocyclic molecules containing two or more linked nitrogens. As always, a key consideration is the desire to achieve the lowest possible degree of sensitivity to unintentional external stimuli, such as shock or impact.

While the presence of several linked nitrogens is frequently associated with instability and/or sensitivity [25], this is not always the case. For example, some derivatives of the tetraazapentalene **6**, such as the tetranitrodibenzo isomers **7**, have surprising stabilities [26]. In an earlier computational analysis [27], we found **6** to be significantly more stable than its isomer **8**, despite the four linked nitrogens in the former. Our study revealed considerable delocalization of charge in **6**, which may be a factor in its stability.

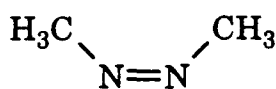
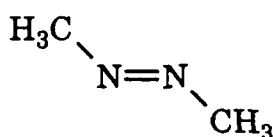
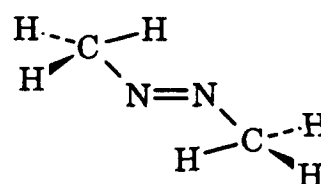


It is well-established, through both experimental and computational evidence [28-34], that there is a degree of instability associated with the presence in a heterocyclic ring of linked doubly-coordinated nitrogens, as in **8**. For example, the measured enthalpies of formation of **9** - **11** show **9** to be approximately 20 kcal/mole less stable than **10** and **11** [35]. The origin of this

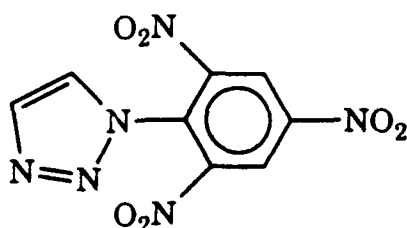
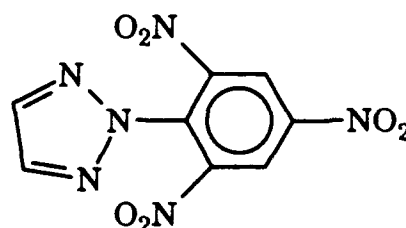
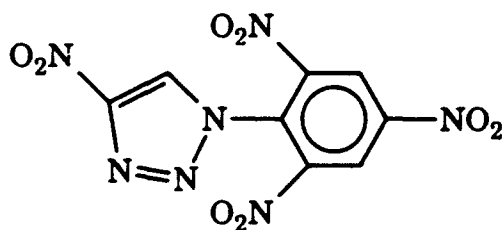
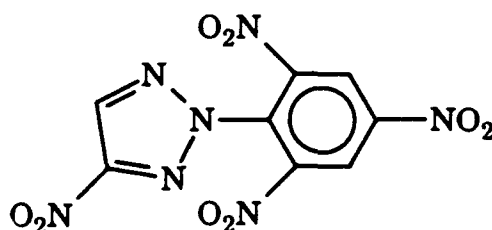


instability may be, at least in part, the proximity of the nitrogen lone pairs when these atoms are forced into a *cis* configuration, as is the case when they form part of a ring [36]. To test this idea, we computed the energies of the *cis* and *trans* isomers **12** and **13**. As anticipated, **12** is 7.9 kcal/mole higher in

energy than the most stable conformer of **13**, in which the methyl groups are rotated so that one hydrogen is in the closest possible proximity to the lone pair on the neighboring nitrogen (**13A**). (All results in this section were obtained with the density functional option of Gaussian 92/DFT, revision G.2 [37], using the Becke exchange [38] and Perdew-Wang correlation [17] functionals and a 6-31G(d,p) basis set. Zero-point energies are included unless otherwise stated.)

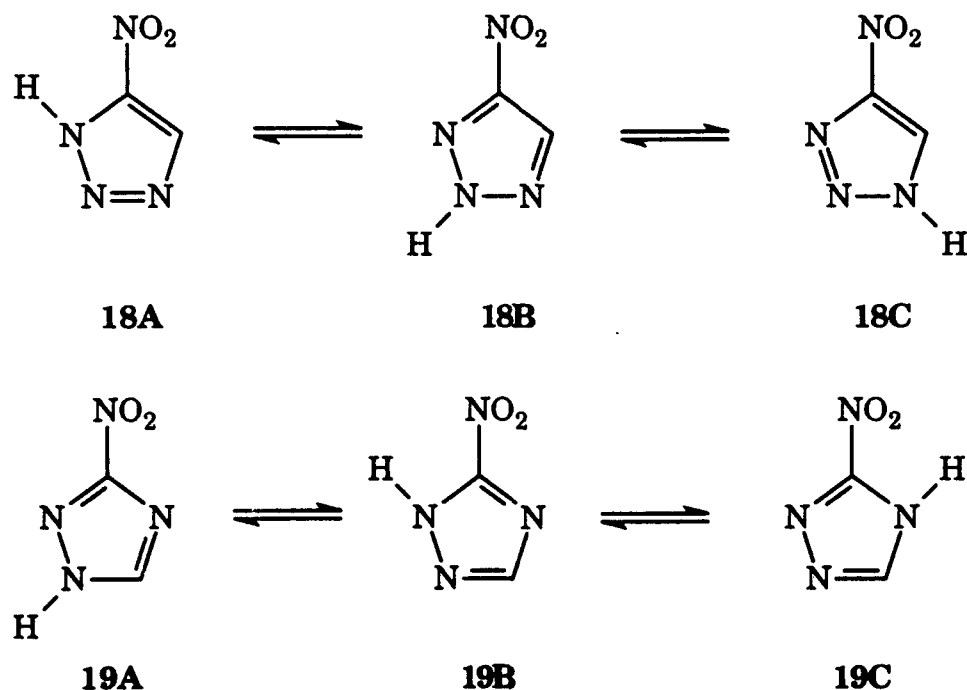
**12****13****13A**

Another source of instability associated with several linked nitrogens may be kinetic. Indeed Storm *et al* have suggested that the considerably greater sensitivity of the picryl triazoles **14** and **16** compared to their isomers **15** and **17** can be attributed to the availability, in **14** and **16**, of a relatively facile decomposition route, through the loss of N₂ from the triazole portion of the molecule [39].

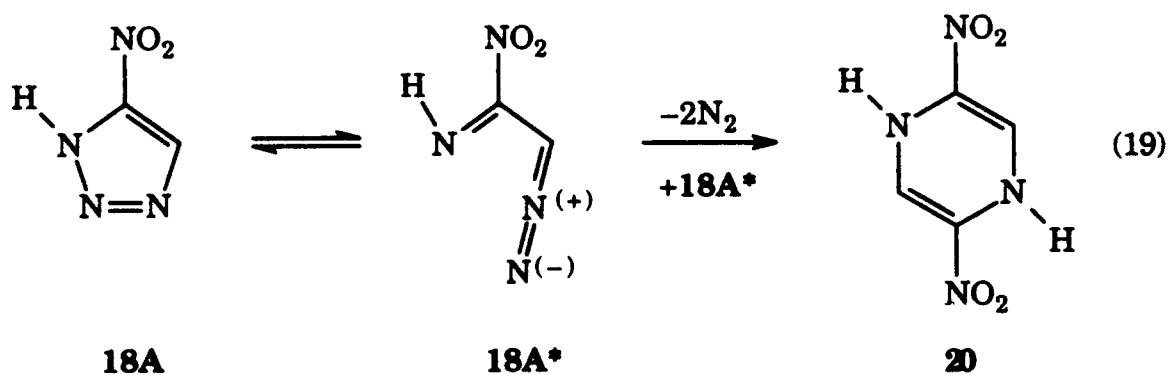
**14****15****16****17**

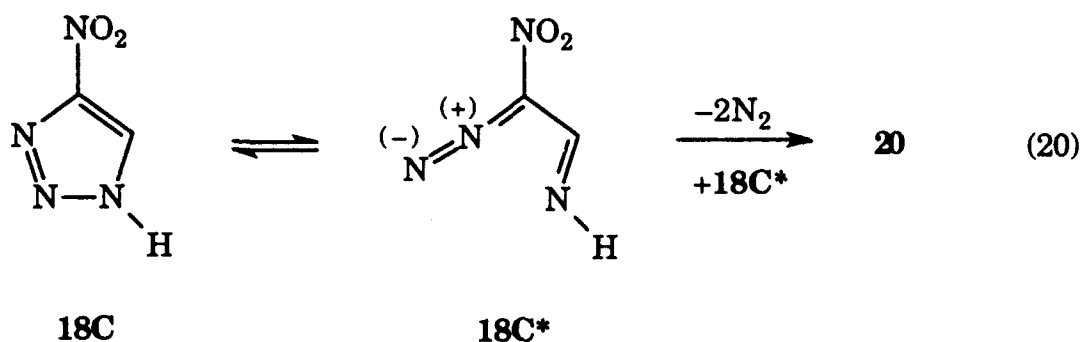
We have investigated this kinetic factor in the case of the nitrotriazole **18**, which is known to be very sensitive to impact [40], in contrast for example to

its isomer **19** which is quite insensitive. Both of these molecules have several tautomeric forms, as shown below.



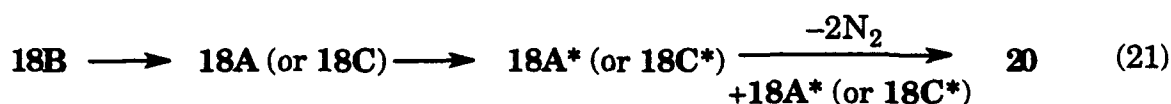
We have shown [41] that a possible decomposition route for **18A** and **18C** is through the formation of the intermediates **18A*** and **18C*** followed by the elimination of two N_2 between two molecules of the intermediate to give the dinitrodihydropyrazine **20**:





Our computed energies for 18A and 18C are virtually the same, as are those of 18A* and 18C*; accordingly the energetics of these two processes, eqs. (19) and (20), are essentially identical. An energy input of approximately 16 kcal/mole is required for the first step, opening the triazole ring to give 18A* or 18C*. However the subsequent formation of the dinitrodihiropyrazine 20 releases 100 kcal per mole produced. Accordingly the reactions described in eqs. (19) and (20) are overall exothermic, with a ΔE of about -34 kcal per mole of the original triazole, 18A or 18C.

The third tautomer, 18B, is unable, for structural reasons, to form an intermediate analogous to 18A* or 18C*. However we found it to be more stable than 18A and 18C by about 3 kcal/mole [41]. Thus one plausible decomposition route for 18 is that represented by eq. (21):



The initiation of this process requires $3 + 16 = 19$ kcal/mole, but there is a net energy release of $\Delta E = -31$ kcal per mole of 18B.

The initial energy input needed for eq. (21), 19 kcal/mole, is relatively low in view of the fact that the decomposition processes of many energetic compounds are believed to begin with the breaking of a C-NO₂ or N-NO₂ bond [42-53]; this typically requires at least 40 kcal/mole, as shown earlier in this chapter and also elsewhere [44, 54, 55]. Furthermore, eq. (21) releases a significant amount of energy which can be used to promote further decomposition. Thus this reaction provides a reasonable interpretation of the high impact sensitivity that has been observed for the nitrotriazole 18. Its insensitive isomer 19, on the other hand, is structurally prevented from undergoing an analogous process.

4. CONCLUSIONS

Nonlocal density functional theory is an effective means for determining the energetics and elucidating the mechanisms of the decomposition processes of molecules of real chemical interest and significance. It should be viewed as another practical tool that is available for this purpose, a useful addition to existing experimental techniques, but with the extremely important advantage that it can be applied to proposed molecules that may not yet have been synthesized or isolated.

ACKNOWLEDGEMENT

We greatly appreciate the support of this work by the Office of Naval Research through contract no. N00014-91-J-4057.

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